A new class of organic molecular magnets

William A. Shelton,[1] Edoardo Aprà,[1] Bobby G. Sumpter,[1] Aldilene Saraiva-Souza,[2]
Antonio G. Souza Filho,[2] Jordan Del Nero,[3] and Vincent Meunier[1]

[1]*Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA.*[*]
[2]*Departamento de Física, Universidade Federal do Ceará, 60455-900, Fortaleza, Ceará, Brazil.*
[3]*Departamento de Física, Universidade Federal do Pará, 66075-110, Belém, Pará, Brazil.*
(Dated: December 3, 2008)

Using detailed first principles calculations, we have found a new class of stable organic molecular magnets based on zwitterionic molecules possessing donor, π bridge, and acceptor groups. These *molecules* are organic molecules containing only C, H and N. The quantum mechanical nature of the magnetic properties originates from the conjugated π bridge (involving only p electrons) where the exchange interactions between electron spin are relatively strong and local and are independent of the length of the π bridge, enabling the easy construction of a molecular magnetic device with specified length.

PACS numbers: 75.50.Xx

Metal-free molecular magnets offer intriguing benefits in terms of cost, weight, and diversity in magnetic properties and ease in processing and synthesis. However most traditional molecular-based magnets are crystals composed of molecular units that contain a variety of metals or radicals[1] that have either a low Curie temperature (T_C) or are unstable due to the processing techniques used to generate them. In the present paper we show that a particular class of organic *molecules*, containing no radicals or metals, can have a stable magnetic ground-state and thus, should have a high Néel temperature (T_N). Moreover, by simply substituting a N with a C atom on the 6-membered ring comprising the betaine molecule (see figure 1) the magnetic state can be changed from antiferrimagntic (Afm) to ferrimagnetic (fm) and it should have a high T_C. Magnetic materials that are purely organic molecules are uncommon since the p-electrons in carbon based materials generally participate in covalent bonds[2]. Our findings indicate that betaine derivatives promise to offer a new class of molecular magnetic materials with diverse potential applications including organic spintronics, information storage and nanoscale sensors.

A limited number of molecular-based magnets have been reported[1] and these are typically composed of organic radicals[3] or mixed coordination compounds containing bridging organic radicals, Prussian Blue type compounds, or charge transfer complexes[4]. For the relatively few organic materials that possess magnetic properties, the Curie temperature (T_C) is generally very low (<36 K) [3][5][6] while those with high T_C typically contain some metallic atoms[7][8][9][2] with the organic molecular part of the crystal acting as exchange pathways. Other allotropes of carbon such as carbon nanofoams[10] and boron-nitride nanotubes[11] have also been reported to exhibit magnetic properties, however either the magnetic properties are very short-lived or they depend on doping and defects to achieve a magnetic state where the stability and strength of the mag-
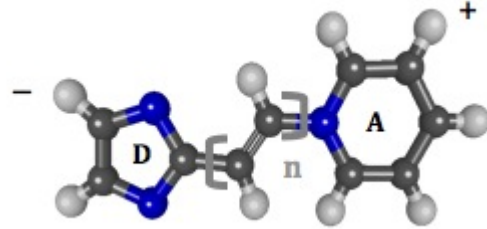

FIG. 1: A zwitterionic betaine molcule with an imidazol donor (D) and a pyridine acceptor (A) separated by alternating C=C bridge.

netism is low since the achieveable doping/defect concentration is quite low[12]. Organic free radicals are natural candidates for magnetic materials, but very few are stable enough to be used as magnetic devices.

While it is clear that some progress towards an organic magnetic material has been made (in particular for graphitic systems), room temperature, air stable and synthetically viable molecules are still lacking. Here we report on a zwitterionic molecular system that is composed entirely of C, N and H and has a magnetic ground-state. The betaine derivatives are zwitterions with a π-conjugated structure whose variable π bridge length separates the donor and acceptor groups[13]. π-conjugated organic molecules are in general good candidates for exhibiting magnetic order,[14] although as discussed above, only a relatively few successful examples have been reported and those have very low T_C. The betaine derivatives are unique because they also have an intrinsic donor and π acceptor at different ends of the molecule. As will be shown in this paper, the magnetic properties of these systems are independent of the bridge length.

The molecular structure for the betaine derivatives is shown in Figure 1. These systems are zwitterions, containing a pyridine acceptor (cation) and imidazole donor (anion) separated by a variable length π-conjugated

$(C_2H_2)_n$ bridge. In this paper, we utilize a combination of *ab initio* techniques for performing fully relaxed total energy calculations using Hartree-Fock (HF), complete active space self consistent field (CASSCF), and density functional theory (DFT) within the framework of the NWChem package[15], to determine the intrinsic character of the ground state for several betaine derivatives. The standard Pople basis set, 6-311G** was used for all calculations, yielding similar results. A hybrid approach was chosen since it is known that using standard density functional theory methods for purely organic π conjugated systems often fail due to the delocalization of the system[16], and 2) an accurate description of electron exchange is necessary for determining magnetic properties. We therefore only report the DFT results obtained using 100% HFX with Perdew-Zunger (PZ) correlation[17]. We note that one can use either PZ or Perdew-Burke-Ernzerhof (PBE)[18] correlation without affecting the magnetic properties since the mechanism responsible for antiferrimagnetism or ferrimagnetism is purely local. To determine the effects of non-dynamical correlation on the magnetic properties, we used CASSCF and the 6-311G** basis set with an active space of up to 14 active electrons and 14 orbitals. The CASSCF results are in good agreement with those obtained from HFX-DFT indicating that the HFX-DFT approach is adequate in describing the correlation in this system.

For the ferromagnetic (FM) state several multiplicities were considered and full geometry optimization was performed where the triplet state was found to be the lowest in energy for the chain lengths considered. We note that the initial antiferromagnetic state relaxes to an antiferrimagnetic state (Afm), and this is the lowest energy state for all bridge lengths examined. Similarly, the initial FM state relaxes to a ferrimagnetic state (fm) for all bridge lengths considered. The results of our investigation demonstrate that the ground state is magnetic, implying that this class of molecules are excellent candidates for the development of new organic magnetic systems.

Restricted open-shell Hartree-Fock (ROHF) calculations for the fm type states were used to rule out potential spin-contamination problems. Higher multiplicity calculations for the fm state were also performed to determine the lowest energy spin state. For the fm type calculations ROHF, UHF and HFX all obtained the triplet state as the ground state spin configuration and no significant effects associated with spin contamination were found.

Table 1 lists the results obtained from geometry optimized calculations using UHF and HFX-PZ. Both yield the same spin configuration ordering with the lowest energy state being antiferrimagnetic (Afm), followed by a ferrimagnetic state (fm) with the highest energy state being non-magnetic (NM). The Afm-fm energy differences (ΔE_{Afm-fm}) listed in table 1 indicate that the Afm ground-state spin structure is exceptionally stable, exhibiting an equivalent temperature

TABLE I: Total energy difference for fully relaxed UHF and HFX-PZ (labeled PZ) simulations for NM, fm and Afm states along with the Afm-NM and Afm-NM and fm-NM total enery differences for UHF and PZ respectively. Atomic units are used and n in Bet$n$, defines the bridge length.

	UHF	ΔE_{Afm-fm}	PZ	ΔE_{Afm-fm}	ΔE_{fm-NM}
$n = 2$					
nm	-624.064		-630.792		
fm	-624.105		-630.811		-0.0187
Afm	-624.117	-0.0118	-630.824	-0.0127	
$n = 4$					
nm	-777.843		-786.352		
fm	-777.919		-786.387		-0.0350
Afm	-777.921	-0.0114	-786.399	-0.0127	
$n = 5$					
nm	-854,734		-864.1333		
fm	-854.812		-864.1744		-0.0411
Afm	-854.823	-0.0113	-864.187	-0.01234	
$n = 6$					
nm	-931.626		-941,916		
fm	-931.713		-941.963		-0.0470
Afm	-931.726	-0.0130	-941.975	-0.0124	
$n = 8$					
nm	-1085.410		-1097.481		
fm	-1085.519		-1097.539		-0.0583
Af	-1085.530	-0.0113	-1097.551	-0.0124	
$n = 10$					
nm	-1239.195		-1253.046		
fm	-1239.322		-1253.116		-0.0693
Afm	-1239.335	-0.0130	-1253.128	-0.0124	

that is well above room temperature. Furthermore, the ΔE_{Afm-fm} is relatively constant as compared to either the ΔE_{Afm-NM} or ΔE_{fm-NM} energy differences. This is about an order of magnitude larger than that typically reported for graphene nanoribbons [19][20].

Figure 2 shows the results for 3 different betaine molecules in the Afm and fm states with bridge lengths of 4, 5, and 10 (see figure 1 for a description of a chain length). The magnetic moments for each C and N site and the total magnetic moments for the chain, 5 and 6 member rings are also displayed (the magnetic moments were calculated using a Mulliken population analysis[21]). For both magnetic states, the magnetic moments of the rings and chains as a function of increasing chain lengths are constant. Interestingly, independent of the magnetic state the chains and rings exhibit an Afm and fm type ordering respectively. For the Afm state, the contributions from the rings approximately cancel each other out, while for the fm state, only the magnetic moment of the 6-membered ring changes and it varies by $\sim 1\mu$B. These results are the same for all chain lengths investigated in this work. Thus, it appears that the magnetism of the system can be viewed as consisting of three nearly independent components, two ring structures and an unsaturated chain.

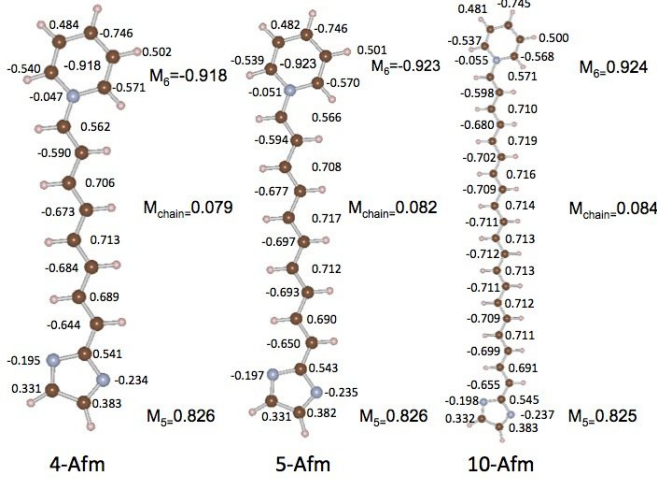The above results imply that the chain length compo-

FIG. 2: The magnetic moments for C and N along with the 5,6 membered ring and C_2H_2 π bridge magnetic moment contributions for chain lengths of 4,5 and 10.
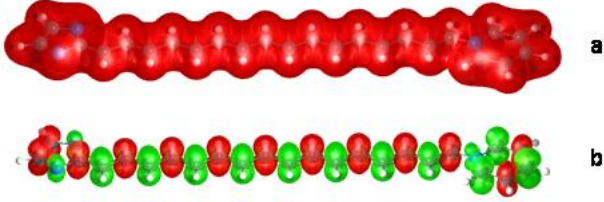

FIG. 3: Figure 3a shows the delocalization of the charge density. Figure 3b displays the spin density showing the strong Heisenberg character.

FIG. 4: ΔE_{Afm-NM} vs C_2H_2 π bridge length.

nent acts as a strongly correlated Afm insulator. This can be seen in the spin density plot shown in figure 3b. Note, that the spin density along the chain contains significant localized Heisenberg spin type character and does not contain any spin dimer like qualities,[22][23][24] while the charge density in figure 3a exhibits strong π-conjugation throughout the molecule. The only fm like coupling occurs in the 5 member ring, which by symmetry must occur. To investigate the magnetic interaction further, a plot of the Afm-NM energy difference (ΔE_{Afm-NM}) vs C_2H_2 chain length is shown in figure 4. For chain lengths of 4 to 10, ΔE_{Afm-NM} decreases linearly with increasing chain length, indicating a strong Heisenberg like behavior with the change in energy being $\propto -J \sum_{\langle ij \rangle} S_i \cdot S_j$, where the summation is restricted to nearest-neighbors. From the spin density and the magnetic moments in figure 2 it is clear that the two rings only interact locally with the first couple of carbon atoms in the chains, which is why there is a slight change in linearity for the chain length of 2. The linear behavior of ΔE_{Afm-NM} with increasing chain length also indicates it is stable and that the chain acts to insulate the two ring structures. This type of screening would account for the change of 1 μ_B
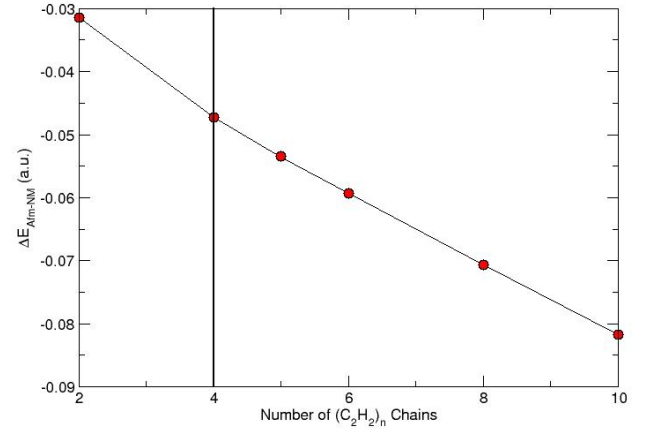
on the 6-membered ring in the fm state. This can be seen from figure 2, where the moments of the two rings are essentially constant with increasing chain length. We also decomposed the eigenvalues (orbital and spin) onto atomic sites for the various chain lengths. The energy for the highest occupied states for the different chain lengths is $\sim$ -0.07 a.u. and essentially constant with increasing chain length. Furthermore, these states are of p_z character and a strong p_z interaction occurs between neighboring spin-up and spin-down states within the chain. This feature taken along with figure 2 accurately illustrates the strong localized Heisenberg spin character. It is also important to note that geometric defects in the chains, such as *cis* conformations, do not disrupt the Afm ordering (results are not shown). While substitutional defects that disrupt the π conjugation on the bridge, such as saturation, will destroy the magnetic character.

The Afm state in this system is different from Andersons theory of superexchange[25] where two next-nearest neighbor transition metal atoms interact through a diamagnetic anion. In addition, C and N atoms have their respective p_x and p_y orbitals shifted down in energy with respect to the p_z orbitals. On the other hand, the p_z spin orbitals are symmetry split, such that, the spin alternates between carbon sites on the chain. This ordering combined with the local nature of the spins lowers the Coulomb energy between sites. The π-conjugation in the rings is strictly local to the individual rings and is maintained through primarily nearest-neighbor interactions with the chain. Interactions with neighbors further down the chain decrease almost exponentially, producing a short-range effective screening, which again highlights the role of the chains to insulate any interactions between the rings, even for short chain lengths.

Additional support for the existence of a magnetic ground state was obtained from CASSCF calculations using various sized active spaces, ranging from 10 electrons and 10 orbitals to 14 electrons and 14 orbitals.

From these calculations it is clear that the natural orbitals show significant partial occupancies, indicating a noteworthy multi-configurational character of the singlet ground state. For Bet6 with an active space of (12,12) the unpaired occupancies are: 1.9448, 1.9332, 1.9242, 1.8799, 1.8570, 1.7075, 0.2933, 0.1525, 0.1202, 0.0739, 0.0523, 0.0613. The unpaired electron density is localized on each C site across the C=C bridge and on the donor and acceptor rings of the molecule. For the larger betaines 7-10, a similar result is found. Larger active space calculations did not change the fact that there is an open shell singlet ground state. The triplet state is higher in energy than the Afm singlet but below the non-magnetic singlet state. These results are consistent with those given in table 1 for the HFX-DFT and UHF calculations.

In this paper we have presented a detailed examination of the fundamental electronic structure of a new class of zwitterionic molecules based on betaine derivatives. The results show that these compounds have a surprisingly strong local Heisenberg type magnetic character that originates from the conjugated bridge in cooperation with the donor-acceptor character of the molecule. The localized behavior found in this system is compatible with the π-conjugation of the components making up the system, thus maintaining the resonant behavior in the systems charge density aiding in its overall stabilization. The Afm state further stabilizes the system because the Coulomb energy is diminished by alternating the spins throughout most of the system. Thus, the stabilization of the system is achieved by the resonating nature of the charge density (kinetic energy) and the localization of the Afm state that results in a lowering of the Coulomb energy. The Afm type ordering found on the conjugated bridge is critical in establishing the short-range local interactions with the donor and acceptor ring structures and the resulting lack of long-range interaction between them. These features are responsible for the stable magnetic configuration as a function of bridge length and could possibly enable the development of a variety of magnetic devices. Furthermore the magnetic character is not disrupted by conformational disorder. Stable room temperature molecular magnetic materials that are purely organic are rather rare and the betaine derivatives promise to offer a new class of molecular magnetic materials with diverse potential applications including organic spintronics, information storage and nanoscale sensors.

* Electronic address: sheltonwajr@ornl.gov; URL: http://www.csm.ornl.gov/ccsg/html/staff/shelton.html

[1] S. Blundell, *Magnetism in Condensed Matter* (Oxford University Press, 2001).

[2] T. Makarova and F. Palacio, eds., *Carbon Based Magnetism: An Overview of the Magnetism of Metal Free Carbon-based Compounds and Materials* (Elsevier Science, 2006).

[3] M. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, M. I. Y. Hosokoshi, M. Takahashi, and M. Kinoshita, Chem. Phys. Lett. **186**, 401 (1991).

[4] J. S. Miller and A. J. Epstein, MRS Bulletin **25**, 21 (2000).

[5] H. W. Kroto, J. R. Heath, and S. C. O. et al., Nature **318**, 162 (1985).

[6] F. Palacio and et. al., Phys. Rev. Lett. **79**, 2336 (1997).

[7] T. L. Makarova, B. Sundqvist, and R. Hohne, Nature **413**, 716 (2001).

[8] A. N. Andriotis, M. Menon, and R. M. Sheetz, Phys. Rev. Lett. **90**, 026801 (2003).

[9] J. A. Chan, B. Montanari, and J. D. Gale, Phys. Rev. B **70**, 041403 (2004).

[10] A. V. Rode, Phys. Rev. B **70**, 054407 (2004).

[11] R. Q. Wu, L. Liu, and G. W. Peng, Appl. Phys. Lett. **86**, 122510 (2005).

[12] J. Miller, J. Calabrese, A. Epstein, R. Bigelow, J. Zhang, and W. Reiff, Journal of the Chemical Society-Chemical Communications pp. 1026–1028 (1986).

[13] A. Saraiva-Souza, B. G. Sumpter, V. Meunier, and et al., J. Phys. Chem. C **112**, 12008 (2008).

[14] A. A. Ovchinnikov, Theoret. Chim. Acta. **47**, 297 (1978).

[15] R. A. Kendall, E. Aprá, D. E. Bernholdt, and et al., Comput. Phys. Commun. **128**, 128 (2000).

[16] S. Hirata, H. Torii, and M. Tasumi, Phys. Rev. B **47**, 11994 (1998).

[17] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[19] D. Jiang, B. G. Sumpter, and S. Dai, J. Chem. Phys. **127**, 124703 (2007).

[20] L. Pisani, J. A. Chan, B. Montanari, and et al., Phys. Rev. B **75**, 064418 (2007).

[21] R. S. Mulliken, J. Chem. Phys. **23**, 1833 (1955).

[22] D. S. Rokhasr and S. A. Kivelson, Phys. Rev. Lett. **61**, 2376 (1988).

[23] P. Fazekas and P. W. Anderson, Philos. Mag. **30**, 423 (1974).

[24] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).

[25] P. W. Anderson, Phys. Rev. **115**, 2 (1959).